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UNIVERSITÀ DEGLI STUDI DI TORINO

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Copper-in-oil Dissolution and Copper-on-paper Deposition Behavior of Mineral Insulating Oils

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ABSTRACT

Copper-in-oil dissolution and copper-on-paper deposition may affect the insulation of oil-filled power transformers, shunt reactors and high voltage bushings. Dissolved copper increases the dielectric losses in oil, and copper deposition can dramatically increase insulating papers' conductivity. The available literature does not report researches where the mechanisms of dissolution of copper in oil and copper deposition on the surface of solid insulation (Kraft paper) have been elucidated.

This study is aimed at the investigation of the tendency of some commercially available unused mineral oils of different compositions to dissolve copper and to deposit it in the cellulose phase. Different conditions of reaction, presence of oxidation inhibitor (of the hindered-phenols family), addition of triazole-type compound (used as corrosion inhibitor) and general oil properties were studied to investigate their influence on copper concentration in oil and onto paper after artificial aging in controlled conditions.

Index Terms — Copper, paper contamination, transformer oil, transformers, non-sulfur corrosion.

1 INTRODUCTION

WHILE the phenomenon of corrosive sulfur in insulating mineral oils is known since long time [1], in the last decade an increasing number of cases of transformers failures has been suspected to be related to corrosion phenomena. Chemical reactions involving both liquid and solid insulation (oil and paper) and copper have been recognized to form copper-containing compounds. Such species may dissolve in the oil, or precipitate as sludge or suspended particles, or form deposits onto the solid insulation (paper tapes, pressboards, etc.) [2, 3].

A well-known cause of corrosion is ascribed to the presence, in the insulating oils, of certain sulfur containing organic compounds, such as dibenzylsulfide (DBDS). These compounds may form partially conductive sulfur salts [4, 5] by reaction with copper (copper sulfides), under the normal operating condition of transformers. Copper sulfide can deposit on the layers of Kraft paper wrapping the copper conductors, or on the surface of bare copper bars [5-9]. As a consequence of the formation of copper sulfides in the paper tapes, a worsening of the dielectric properties of solid insulation occurs, with possible electrical failure between the conductors (turn-to-turn short circuit). On the other hand, the

increase of the thickness of copper sulfide layer may cause the detachment of conductive particles from the bare copper surface. Some researchers [10] postulated that copper could migrate towards the cellulose in soluble forms, before binding to sulfur and forming insoluble conductive compounds. This hypothesis might explain the presence of deposits on the layers of Kraft paper wrapping the copper conductors, found in some scrapped units [5, 8, 9].

Even if DBDS is the most frequently occurring molecule found in oils having a positive response to corrosion tests (i.e. method ASTM D1275 B and method IEC 62535), the capability of some oils to transfer copper onto the insulating paper tapes or to dissolve copper has been noticed even in oils where DBDS is absent. Also, a recent case history [11] has shown that copper sulfide may be formed on papers wrapping enameled copper, if naked copper is available otherwise (i.e. from bus bars) and the oil can transfer copper onto the cellulose.

Hence, more extensive studies on the tendency to dissolve and deposit copper also by oils not containing corrosive sulfur compounds are necessary. Understanding the conditions in which the corrosion can be limited (or enhanced) is a very important task

for risk assessment and mitigation in power transformers. For this purpose it is fundamental to establish the influence of factors such as temperature, presence of oxygen, and oil characteristics. Saha et al. [12] demonstrated that high temperatures markedly accelerate the ageing processes (in accordance with Arrhenius equation) of oil and paper windings inside the transformer, so damaging insulators dielectric properties. Moreover, oil dielectric properties were recently correlated to the physical form in which copper is present in oil [13]. Other works [14-16] have elucidated that copper dissolves in oil mainly through the formation of metal hydroxide species as well as through the reaction with other compounds present in the oil. In these papers, the fundamental role of oxygen into dissolution and deposition processes is underlined, but no information is provided on the influence of other oil parameters. Also, oil's additives (i.e. substances added to the oil in order to improve specific characteristics that are not inherently sufficient for the purpose to which the same oil is addressed) may influence its tendency to dissolve or deposit copper. The role and classification of additives in mineral insulating oils may lead to some misunderstanding, due to the fact that some of them may cover more than one scope. As an example, triazole-type compounds are used primarily as electrostatic charging depressants, but they also may improve oxidation stability, or be used as corrosion inhibitors. For better clarity, in this work we have followed the definitions reported in standard IEC 60296:2012, clause 3. According to this standard, passivators are included among the additives used in mineral insulating oils, and defined as metal passivators additives that may also improve oxidation stability, or act as corrosion inhibitors.

Recent studies [16, 17] investigated the long-term effects of metal passivators on the inhibition of copper sulphide formation; nevertheless, to the best of the authors' knowledge, the effect of triazole-type additives on copper dissolution in oils not containing corrosive sulfur species has not yet been investigated, despite they are largely used for purposes other than copper protection against corrosive sulfur (e.g.: oil's electrostatic charging depressants). Other recent works [18,19] investigated the deposition of copper on paper in the presence of different oxygen percentages, for uninhibited (< 0.01 % by weight of 2,6-di-tert-butyl-p-cresol, DBPC) and inhibited (up to 0.4 % by weight of DBPC) oils. Even if these studies have revealed that DBPC accelerates the formation of copper deposits on insulating paper, all tests were conducted on oils containing DBDS; thus, the influence of phenolic oxidation inhibitors (belonging to the family of sterically hindered phenols) on copper dissolution is not known, yet.

In the light of these considerations, the aim of this research was the investigation of the tendency of oil to dissolve copper and to deposit it on paper as a function of oil characteristics and atmosphere conditions. In particular, unused mineral oils available on the market, with different chemical and physical properties, were fortified with known amount of two of the most widely used oil additives: Irgamet[®]39 and DBPC, to clarify their role in the dissolution and deposition processes. The effects of temperature and atmosphere on corrosion processes were also assessed.

2 EXPERIMENTAL

2.1 MINERAL OILS

Eight unused oils were purchased from those available in the market to study their copper dissolution and deposition tendency (CDT) into oil and onto paper respectively. They were: (1): Hyvolt II (Ergon); (2): Hyvolt III (Ergon); (3): ITE360 (Agip); (4): Diala B (Shell); (5): Diala D (Shell); (6): Diala DX (Shell); (7): Libra (Nynas); (8): Gemini X (Nynas). They were characterized in terms of known additives, total aromatics content, density, viscosity and flash point as described in Table I.

Table 1. Characterization of the selected unused oils.

Oils		Parameters of characterization				
#	Oil Name	FP ^a	ρ ^b	AC ^c	ν ^d	DBPC ^e
1	Ergon Hyvolt II	140,5	876	9,37	9,51	0,207
2	Ergon Hyvolt III	137,5	866	3,12	8,63	0,279
3	Agip ITE360	142,5	880	12,14	9,64	< 0,01
4	Shell Diala B	148,5	875	5,73	11,08	< 0,01
5	Shell Diala D	140,5	873	9,29	8,23	< 0,01
6	Shell Diala DX	140,5	871	4,59	8,24	0,255
7	Nynas Libra	150,5	872	8,47	9,79	< 0,01
8	Nynas Gemini X	146,5	877	7,49	8,70	0,272

a. Flash Point PMCC, °C; b. Density at 20 °C, kg/m³; c. Aromatic Content, % m/m;

d. kinematic viscosity cSt at 40°C, Oxidation inhibitor content (Di-tert-Butyl-Para-Cresol, DBPC), % m/m.

In particular, this selection included four inhibited (according to IEC 60296:2012 definition) oils: Hyvolt II, Hyvolt III, Diala DX, Gemini X; and four uninhibited (according to IEC 60296:2012 definition) oils: ITE360, Diala D, Diala B, Libra.

For ITE360 and Gemini X oils, the presence of the metal deactivator CIBA Irgamet[®]30 was detected in concentration of 15 mg/kg and 7.2 mg/kg, respectively. None of the eight oils contains the most commonly used triazole-type additive (Irgamet[®]39). The density of these selected oils ranges from 866 to 880 kg/m³ at 20 °C, in agreement with accepted value for unused mineral oils (< 895 kg/m³ at 20 °C). The measured flash points are consistent with the value usually achieved by mineral oils (> 135 °C). The samples widely differ in kinematic viscosity (at 40 °C), that ranges from 8.2 (Diala D and Diala DX) to 11.1 cSt (Diala B); total aromatic content also vary in a quite large range, from 3.1% (Hyvolt III) to 12.1% (ITE 360). The oil characterization underlines the heterogeneous composition of the samples chosen.

2.2 COPPER DISSOLUTION AND DEPOSITION TENDENCY

In order to evaluate the concentration of copper dissolved or deposited by the unused oils, a CDT method (Copper Deposition and Dissolution Tendency Test) was developed. In detail, a copper wire of known diameter (15 cm² surface area) divided into small pieces (about 1 cm each), and 30 cm² of Kraft paper divided into 8 fan-shaped parts were put in contact with 12 g of each oil. The test was performed in 20 ml vials sealed with a PTFE/butyl rubber septum, and heated, under continuous stirring, for 72 h at different reaction conditions, as described in the following sections. After the process completion, oil samples were centrifuged to remove the suspended particles of large diameter potentially formed as a

consequence of the oil's oxidation, and copper in oil content was determined according to a modified ASTM D 7151 procedure [20]. Copper deposited onto the paper's surface was quantitatively determined by ICP-OES after cellulose mineralization, previously washed with isooctane and cyclohexane, in an acidic-oxidative aqueous solution (12 ml of $\text{HNO}_3/\text{H}_2\text{O}_2$ 5:2 v/v). Before ICP analysis, the digested samples were filtered with Polyamide filter (0.45 μm), and diluted 1:10 (v/v) with HPLC grade water.

3 RESULTS AND DISCUSSION

To study the copper in oil dissolution and deposition tendency on paper (CDT) and to get a more thorough insight on the correlations between the working conditions of a transformer and the tendency of its oil to dissolve or deposit metals, the effect of temperature, additives and atmosphere was investigated. Other influencing parameters could be studied (e.g.: effect of electric field), but they were not considered in this work.

3.1 EFFECT OF TEMPERATURE

The effect of temperature on the tendency of unused oils to dissolve and deposit copper was investigated in a range 80 to 140 °C. Tests were performed at 80, 100, 120 and 140 °C. These temperature levels also include conditions beyond the maximum allowed operating temperature (according to IEC Loading Guide, 105 °C), and were chosen to accelerate the corrosion process. Experiments were performed as described in the Experimental section.

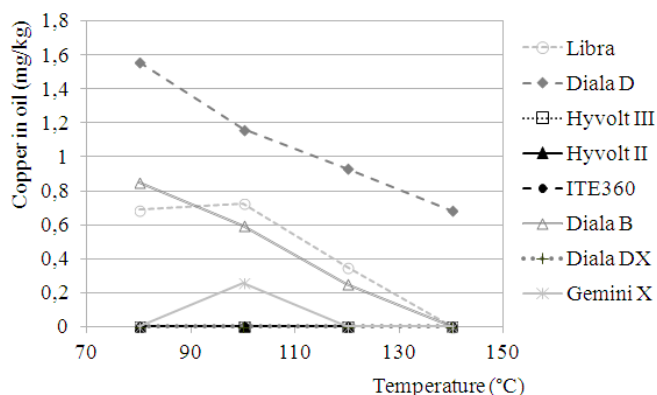


Figure 1. Correlation between copper in oil and temperature applied. Three replicates for each condition, RSD% 0 ÷ 26.4. AC = Aromatic Content, expressed in % m/m .

Figure 1 shows that, in case of uninhibited oils (Diala D, Libra, Diala B) the dissolution of copper in oil basically decreases by increasing temperatures. The opposite was found in case of inhibited (Hyvolt II, Hyvolt III, Diala DX), where copper content was constant and below the instrumental detection limit (29.3 ppb) [20], indicating that inhibited oils do not appreciably dissolve copper under the explored experimental conditions. For uninhibited oils (Libra, Diala D, Diala B), results in Figure 1 suggest that dissolved copper formation is inversely proportional to temperature. It is noteworthy that ITE 360 oil, although not containing DBPC, does not form

detectable dissolved copper even under harsh reaction conditions. This behavior may be the effect of the presence of Irgamet®30 as metal deactivator (15 mg/kg).

Accordingly with Arrhenius' equation, and with previous works that confirmed that high temperatures markedly accelerate the ageing processes of oil and paper windings into the transformer [15], an increasing formation of sludge and deposits observed in case of uninhibited oil at higher temperatures may result in the precipitation of insoluble forms of copper, under the reaction conditions of these experiments. This may explain the reduction of dissolved copper with the increase of temperature: copper is trapped into sludge particles and is not detected by ICP-OES technique. It can thus be expected that some copper precipitates in the sludge formed by oxidation. This aspect will be treated later in this paper (see "Effect of oxygen" section).

On the contrary, the presence of the oxidation inhibitor slows down the ageing phenomenon and hamper the subsequent sludge formation. The negligible formation of dissolved copper in inhibited oils may be ascribed to the absence of acidic compounds usually formed during the oxidation.

Total aromatic content seems also to have a certain effect on the amount of dissolved copper (at least for uninhibited oils). In fact, for those insulating oils that show a tendency to dissolve copper, metal content in oil increases with the increase of total aromatic content. This behavior was also observed by Lukic [15], who underlined the tendency of aromatic compounds to form stable benzylic radicals, that may interact in the copper oxidation and complexation processes. This suggests that the characterization of aromatics (e.g.: type, presence of heteroatoms) might be an interesting investigation tool for the future.

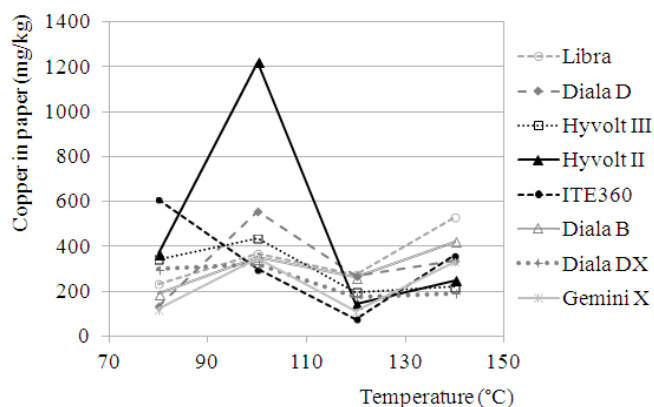


Figure 2. Correlation between temperature applied and copper concentration in paper found after wet digestion. 3 replicates for each condition; RSD% 9.1 ÷ 23.2.

The effect of temperature on the transfer of copper into the paper phase is less straightforward (Figure 2). In fact, with the exception of Hyvolt II oil, that deposited much more copper at 100 °C (1200 mg/kg) under the applied reaction conditions, all the other oils deposit a low and fairly constant copper amount (350 mg/kg average value) in the paper.

3.2 EFFECT OF DBPC

Considering the effect of the presence of an oxidation inhibitor on the copper dissolution process, as previously described, the effect of DBPC was further investigated. In detail, two uninhibited oils (ITE360 and Diala D) were fortified with increasing concentrations of DBPC: 0.05% (amount typical for trace inhibited, according to IEC 60296 definition), 0.1, and 0.3% (amount commonly added full inhibited oil, according to IEC 60296 definition). All tests were performed at 100 °C, with a duration of 72 hours, in the conditions described in paragraph 2.2. This value is still below the maximum oil temperature in a transformer working at normal operative conditions (105 °C), accordingly with IEC loading guide.

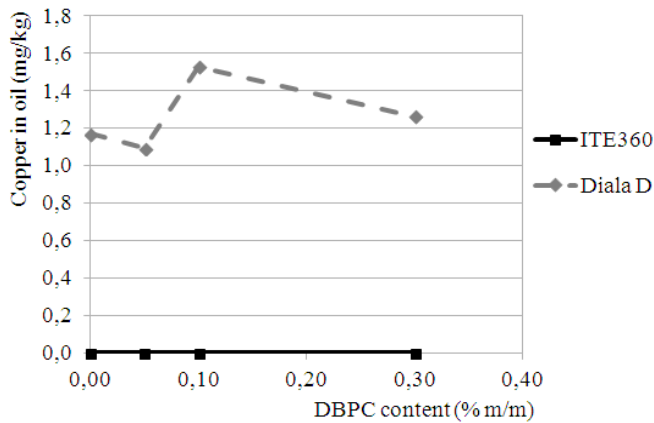


Figure 3. Correlation between copper concentration in oil and % of DBPC added.

As shown in Figure 3, the presence of DBPC does not significantly influence the amount of copper dissolved, which remains constant at about 1.3 mg/kg under the applied experimental conditions. ITE 360 oil does not transfer copper into oil-phase, possibly due to the presence of a metal deactivator, as previously discussed.

On the contrary, a significant relationship was highlighted between the increase of inhibitor (DBPC) concentration and the amount of copper deposited in the paper-phase, which increases as well (Figure 4). This behavior, in agreement with what was observed by Kawarai [19], can be explained by the possible formation of a copper-DBPC-complex, that increases mobility of copper in oil, so favoring its transfer onto the paper surface. Nevertheless, this mobility did not lead to increased copper concentration in oil phase, since Cu appears to be transferred mostly into the paper phase. This may be explained by the partition coefficient of polar compounds (such as copper complexes) between oil and paper phases: cellulose is more polar than oil, and dissolved copper species tend consequently to accumulate on the paper.

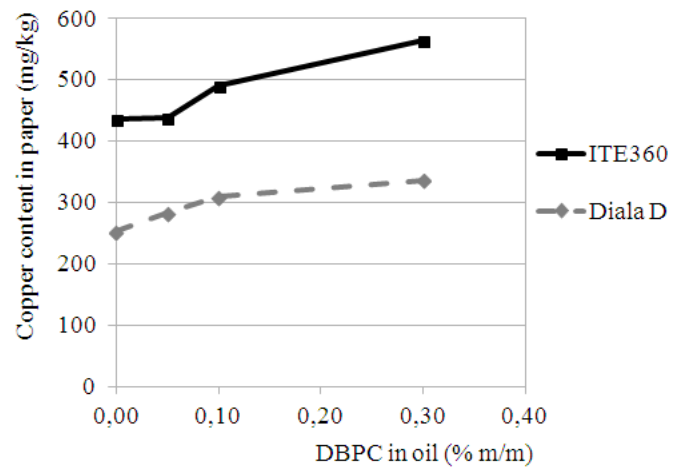


Figure 4. Correlation between DBPC content in oil and copper concentration in paper found after wet digestion.

3.3 EFFECT OF IRGAMET®39.

As shown in recent works [16], oils containing Irgamet®39 can alter the dissolution process of copper in oil and its deposition onto the paper insulation. To investigate these phenomena, Irgamet®39 was added to an inhibited oil (Hyvolt II, containing DBPC as antioxidant) and to an uninhibited oil (Diala D, declared as uninhibited).

Irgamet®39 was added at concentrations of: 50 ppm, 100 ppm (concentration usually added to an oil to reduce the effects of corrosive sulfur), and 250 ppm (maximum added concentration). The copper dissolution and deposition tendency was studied at the conditions described in the experimental section, fixing again the temperature at 100 °C.

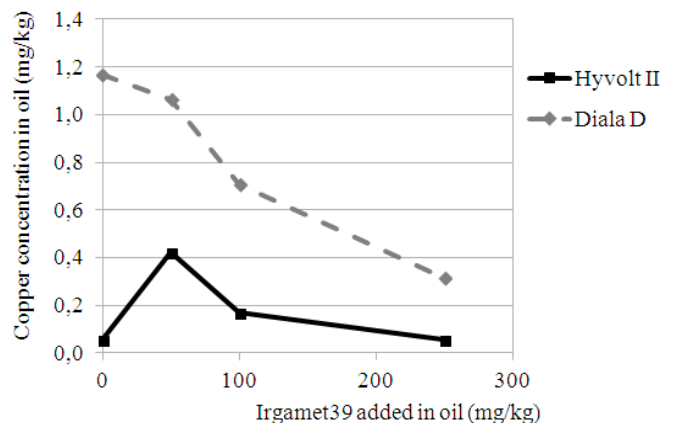


Figure 5. Correlation between copper concentration in oil and concentration of Irgamet®39.

As expected, due to the shielding role of Irgamet®39 towards the conductor, the amount of copper dissolved in oil decreases with the increase of Irgamet®39 content (Figure 5) under the applied experimental conditions. Although both the inhibited and the uninhibited oils show this behavior, in case of Hyvolt II (containing DBPC), the amount of copper in oil is lower if compared with Diala D, which does not contain DBPC. This result is in agreement with what was previously observed and discussed, where the presence of an inhibitor

(DBPC) was related to a minor tendency to dissolve metal.

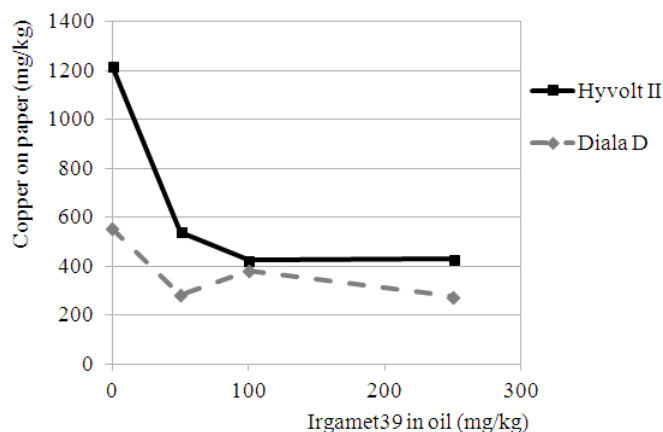


Figure 6. Correlation between Irgamet[®]39 concentration and copper concentration in paper found after wet digestion.

The results obtained studying the effects of Irgamet[®]39 on copper deposited onto paper were definitely unexpected. Although an overall decrease of copper content in the paper was observed for increasing Irgamet[®]39 concentration (see Figure 6), the behavior of the two oils is reversed in respect to what previously observed for copper in oil. In particular, the oil inhibited with DBPC has a higher tendency to deposit copper: this result confirms the hypothesis postulated (see “Effect of inhibitor (DBPC)” section) of the formation of a Cu-DBPC complex that favors the transfer of metal onto the paper surface.

3.4 EFFECT OF OXYGEN

Since the transformers can operate either in a hermetically sealed or in an air exposed configuration [21], an important parameter to take into account is the presence and availability of oxygen. In particular, the reactions occurring under totally inert atmosphere (obtained with Ar), partially oxidative atmosphere (obtained with air) and highly oxidative atmosphere (obtained with oxygen) were evaluated for Hyvolt II (inhibited—with DBPC) and Diala D (uninhibited—without DBPC). These two oils were chosen for the comparison, because they have a similar total aromatics content, thus the effect of this parameter can be probably considered as negligible.

Temperature was fixed at 100 °C, while a continuous and constant gas flow was applied during the 72 hours reaction time. The results obtained, depicted in Figure 7, indicate that, at increasing oxidative conditions, the concentration of copper in oil decreases in the case of uninhibited oil (Diala D, containing DBPC), while it is almost constant, and even slightly increasing, in case of oil containing DBPC. In particular, higher concentration of metal revealed in inert condition in case of uninhibited oil, confirms that the absence of DBPC favors the dissolution of copper in oil, at least in the case of low or null oxygen availability. At partially oxidative conditions (air) the oils appear to have the same behavior, but the difference between oil with and without DBPC is

definitively less. In the case of an oxidative environment (as is the case of free breathing transformers), the trend is totally reversed. In this case, sludge was observed for Diala D, possibly due to the fact that oils without oxidation inhibitors are completely exposed to the accelerated oxidation processes, with the subsequent precipitation of copper (most probably in the form of copper oxides and insoluble complexes). If the oil contains DBPC, an environment saturated in oxygen appears to accelerate copper dissolution. Comparing the results of the experiments performed under the three conditions above described, it can be supposed that the oil without DBPC (Diala D) has a major tendency to dissolve copper, if compared to the other oil with DBPC (Hyvolt II), but this behavior may be masked by the presence of an oxidative atmosphere. In fact, the increasing availability of oxygen seems to cause the inversion of the dissolution tendency, possibly due to the lower oxidation resistance of Diala D, that is more prone to form sludge during the reaction. The sludge can trap the copper and induce its precipitation, thus reducing the amount of detectable dissolved copper in the oil.

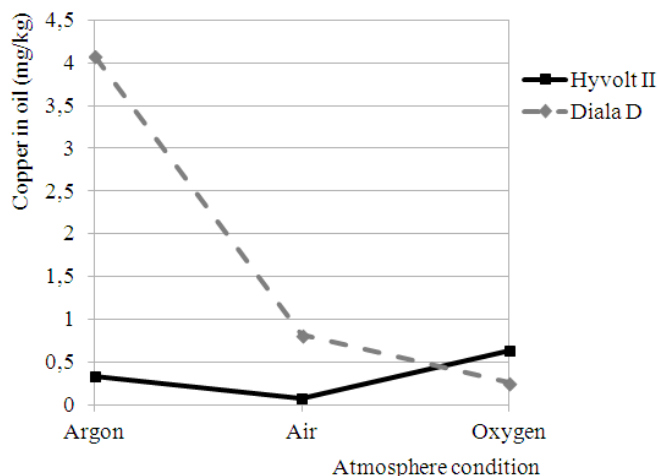


Figure 7. Copper in oil concentrations found after ageing under non-oxidative, partially oxidative and highly oxidative conditions.

To verify this hypothesis, Diala D oil resulting from the reaction under highly oxidative conditions experiment was centrifuged, digesting the sludge retrieved from the reaction vial, and the supernatant oil, by microwave-assisted mineralization. As shown in Figure 8, a relevant amount of copper was formed in the oil, but it was mostly in an insoluble form (probably as copper oxide), as it can be perceived observing that the copper concentration measured in the oil after mineralization is much higher than the concentration measured by direct ICP injection. Indeed, 7 mg/kg of copper were detected after mineralization, whilst a negligible amount of copper can be detected by direct injection with ICP/OES technique. Moreover, the concentration of copper found in the sludge, was very close to the concentration measured in the oil at inert condition (4 ppm), confirming the precipitation of copper oxide in oxidative atmosphere.

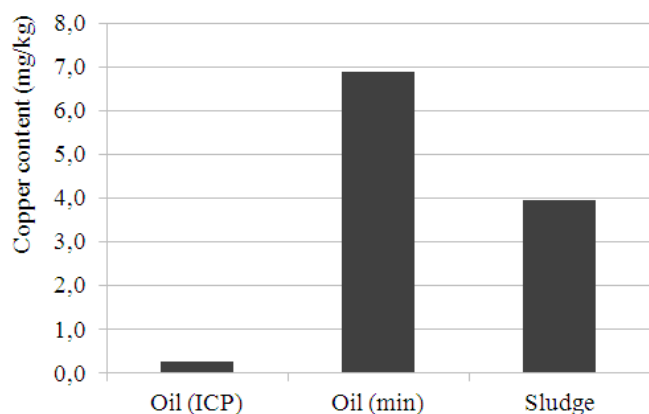


Figure 8. Copper content in the supernatant oil (measured by ICP/OES direct injection and after mineralization) and in the sludge formed after oxidation of Diala D oil.

The relation between the increase of oxygen percentage and deposition of copper onto paper is of more difficult interpretation. In fact, both in the case of an oil inhibited with DBPC and another one uninhibited (without DBPC) (Figure 9), deposition of copper on the paper was maximum under air atmosphere in respect to a totally non-oxidative (Argon) and a fully oxidative atmosphere (Oxygen). This behavior is in agreement with previous studies [9], that correlated e.g. Cu_2S deposition onto paper with the oxygen fraction involved in the reaction. Cu_2S deposition was found to be maximized at intermediate oxygen content.

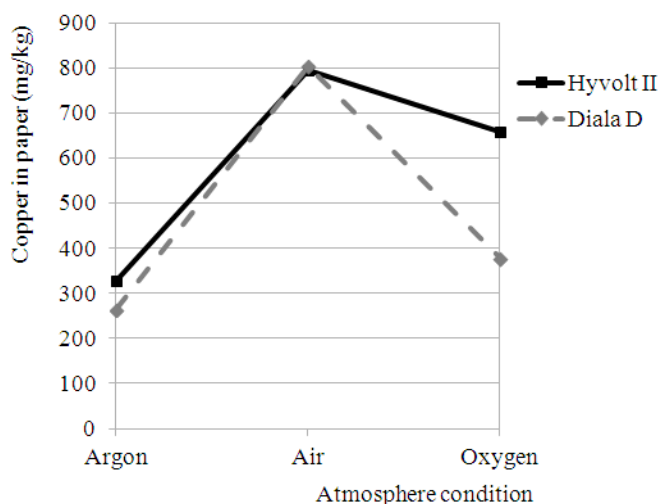


Figure 9. Copper in paper concentrations found after ageing under non-oxidative, partially oxidative and highly oxidative conditions.

At saturated oxidative conditions the concentration of copper in paper decreased for both the oils. This phenomenon is enhanced for Diala D (uninhibited); a possible explanation is that the metal precipitates as sludge, so preventing its transfer onto paper. It is remarkable that, as postulated in previous sections, inhibited oil (Hyvolt II) deposited more copper onto paper if compared with uninhibited oil, so giving an additional evidence of the formation of a Cu-DBPC complex, which promotes the copper adsorption onto paper.

The results obtained so far stress the importance of the environment in which the transformer operates. Therefore, the

effect of temperature on copper dissolution was finally investigated, under inert conditions (argon). The graph reported in Figure 10 shows a totally different behavior if compared to the trend depicted in Figure 1 (atmosphere not controlled). Uninhibited oils (i.e. oils without DBPC) are still the ones having the higher tendency to dissolve copper, but this tendency increases with temperature. In fact, since high temperatures markedly accelerate the oxidation processes in oil, a totally oxygen-free atmosphere may hamper the copper precipitation as oxides compounds, thus promoting the formation of dissolved metal in oil, particularly for oils not containing DBPC (less protected from oxidation).

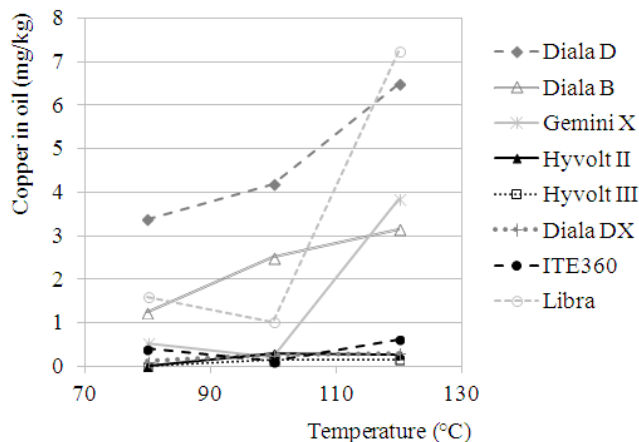


Figure 10. Copper in oil content as a function of temperature, under inert atmospheric conditions (Argon).

Finally, it must be highlighted that ITE360 is the unique uninhibited oil forming low concentrations of dissolved copper. This might be the effect of the presence of a metal deactivator, in agreement with what previously stated (see “Effect of Temperature” section), but it cannot be excluded that it depends on the composition of the base oil.

4 CONCLUSION

Differently from the studies currently available in literature, which describe results of copper dissolution and deposition mostly in a qualitative way, the study here proposed reports quantitative information on the observed phenomena, under the applied reaction conditions.

Dissolved copper in oil formation strongly depends on many parameters. Temperature, above all, accelerates the copper dissolution reactions. Nevertheless, its actual effect is strongly dependent on the presence of oxygen: under inert (non-oxidative) atmosphere the measured dissolved copper increases with temperature, especially for uninhibited oils (not containing DBPC). When oxygen is available, on the other hand, copper is mostly trapped in the sludge, or tends to precipitate, e.g. in the form of copper oxides, leading to a opposite behavior (the amount of copper in oil is inversely proportional to temperature). Most probably, aromatic content can also favor copper dissolution in oil *via* metal-complex formation. Nevertheless, it was not possible to evaluate this effect due to the difficulties to fortify an oil with aromatic

compounds similar to the ones present in mineral oils. Inhibitor's (i.e. DBPC) concentration does not apparently influence dissolved copper formation. Irgamet[®]39 reduces dissolved copper formation as a consequence of their protective action on copper surfaces. Accumulation of copper onto the paper surfaces is also influenced by temperature and oxygen, but in a more complex way. The deposition of copper species on the solid insulation may pass through several pathways, including the adsorption of dissolved copper compounds in the polar cellulose matrix, and the incorporation of sludge-trapped copper species. This makes difficult to evaluate the correlated action of temperature and oxygen, but it appears quite clear that higher temperatures lead to a generally higher copper dissolution, and that copper fate depends on the capability of the oil to resist to oxidation and to limit the sludge formation. It seems anyway that the process is enhanced with intermediate oxygen availability, and is slower under inert atmosphere or strongly oxidative atmosphere. While Irgamet[®]39 appears to decrease the copper-on-paper accumulation, by mean of their shielding action on copper surfaces, DBPC presence may increase the rate of formation of copper deposits on paper. In this case, since DBPC protects the oil from oxidation, the mechanism of copper-complexes adsorption on paper should be more realistic.

As a conclusion, in terms of copper dissolution and deposition, the use of DBPC-inhibited oils should be preferred, even if it slightly increases the capability of the oil to transfer copper in soluble forms. Triazole-type passivators also have a protective action on copper and can reduce the dissolution effect. This may depend on the multiple role that triazole-type compounds may play in the mineral oil: according to standard IEC 60296 definitions they are metal passivator (meaning that they can protect the metal surface by forming a stable coating), but they may also improve oxidation stability (probably by reducing the catalytic effect of copper in oxidation reactions), or be used as corrosion inhibitors (protecting the copper from the corrosive action of sulfur compounds).

Finally, transformer design that reduces oxygen access (e.g. membrane-type conservators, nitrogen blanketed conservators) will lead to lower copper dissolution along the transformer's life.

APPENDIX

For copper quantification a 710-ES Varian (Lexington MA, USA) Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) was used. The spectrometer is provided with a radio frequency generator (40 MHz) and a Charge Coupled Device detector. For aqueous solutions, sample introduction was performed by a glass cyclonic spray chamber and a concentric glass nebulizer, whereas for organic samples, a Sturman-Masters spray chamber was coupled with a V-groove nebulizer. To facilitate the analysis of volatile organics, an AGM-1 (Auxiliary Gas Module) was used to introduce a controlled amount of oxygen in the argon plasma. The ICP-instrumental conditions used for analysis of organic and aqueous samples are described in ref. [20].

A XP205DR semi-micron (5 decimal digits) balance (Mettler Toledo, Greifensee, Switzerland) was used to weigh paper before digestion.

A Discover SP-D (CEM, BG, Italy) microwave digester provided with autosampler was used for oil and sludge mineralization. This microwave digestion system is characterized by faster mineralization times and absence of cross-contamination phenomena due to the use of disposable pyrex vessels [22].

ICP-OES method was calibrated with organic copper standard solutions prepared in a technical oil (Libra, Nynas, Stockholm, Sweden) from a 5000 µg/g organo-metallic reference standard copper in hydrocarbon oil at 75 cSt (Accustandard, CT, USA). Metryk 180 (Brenntag, Belgium), a clear fluid commonly named *isopar*, was used to dilute Cu solutions and oil samples. Isooctane (Panreac, Barcelona, Spain) and cyclohexane (Panreac, Barcelona, Spain) were used to wash paper before mineralization.

Chromasolv HPLC water (Panreac Quimica, Barcellona, Spain) was used for dilution of aqueous standards and samples. Nitric acid (65%, Panreac, Spain) and hydrogen peroxide (30%, Fluka, MO, USA) were used for paper mineralization. Aqueous copper standard solutions were prepared from a 100µg/ml ICP Multi-Element standard (AccuTrace Reference Standard, CT, USA).

2,6-di-tert-butyl-p-cresol (DBPC, 99%) and Irgamet[®]39 were from Fluka (MO, USA) and Ciba (BASF, Ludwigshafen, Germany) respectively.

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